



Ni-based anode-supported Al₂O₃-doped-Y₂O₃-stabilized ZrO₂ thin electrolyte solid oxide fuel cells with Y₂O₃-stabilized ZrO₂ buffer layer

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HIGHLIGHTS

- In anode-supported SOFCs, Al₂O₃ is doped into YSZ electrolyte as sintering aid.
- 1 wt.% Al₂O₃ doping can reduce the sintering temperature of YSZ to 1573 K.
- The output of cell is improved with reduced sintering temperature.
- A buffer layer is introduced between the Al₂O₃-doped-YSZ electrolyte and anode.
- Buffer layer prevents Al₂O₃ and NiO from forming non-conductive NiAl₂O₄.

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ABSTRACT

In order to reduce the sintering temperature of Ni-based anode-supported thin 8 mol% yttria-stabilized zirconia (YSZ) electrolyte solid oxide fuel cells (SOFCs), alumina, with a weight percent of 1, 3, 5, and 7, is respectively doped into YSZ as sintering aid. A pure YSZ buffer layer is introduced between the Al₂O₃-doped-YSZ electrolyte and Ni-YSZ anode, to prevent Al₂O₃ and NiO from forming non-conductive spinel NiAl₂O₄. The experimental results show that doping proper amount of Al₂O₃ doping can reduce the sintering temperature of YSZ, e.g., 1 wt.% doping decreases the temperature from 1673 K to 1573 K. Anode-supported SOFCs are prepared with Al₂O₃-doped-YSZ electrolytes sintered at different temperatures. Electrochemical characterization of the SOFCs shows that the single cell with 1 wt.% alumina-doped YSZ electrolyte sintered at 1573 K gives the highest output. The effect of alumina doping on sintering behavior and electrical performance of YSZ is discussed in detail.

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1. Introduction

The solid oxide fuel cell (SOFC) is an all-solid-state energy conversion device that produces electricity by electrochemically combining fuels and oxidant gases through an ionic conducting oxide [1]. It has received considerable attention for its high efficiency, low impact on environment, fuel flexibility and all-solid-state structure. In the foreseeable future, SOFC is a promising alternative to conventional electricity generation technology for

applications in distributed power station, back-up and even portable power sources [2].

Up to date, the most commonly used SOFC materials are yttria-stabilized zirconia (YSZ) for the electrolyte, Ni-YSZ cermet for the anode, and composite of strontium doped lanthanum manganate (LSM) and YSZ for the cathode. There are three basic configurations of SOFCs, electrolyte-supported, cathode-supported, and anode-supported, among which, anode-supported SOFCs, with a porous anode as the thickest component (0.3–1.5 mm) and a thin layer of dense electrolyte (10–20 μm) deposited on the anode, give the highest performance [3]. Typical process for fabricating Ni-YSZ anode-supported thin YSZ electrolyte SOFCs involves three steps: First, the anode substrate is prepared and pre-fired at 1273 K–1473 K. Then, the thin electrolyte layer is coated on the pre-fired anode substrate and the bi-layer is co-sintered at 1673 K.

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Finally, an LSM–YSZ composite cathode layer is applied on the surface of the electrolyte and sintered at 1373–1523 K. In the second step, a temperature as high as 1673 K is generally necessary to densify the electrolyte so that the fuel and oxidant can be effectively isolated during SOFC operation [4–6]. High sintering temperature brings some drawbacks: it increases the energy consumption and cost; it causes over-sintering of the anode, resulting in decrease of porosity and specific surface area, leading to deactivation of anode. Therefore, lowering the sintering temperature can not only reduce the fabrication cost but also enhance the cell performance.

Reducing sintering temperature of YSZ has been pursued for a long time. Among a variety of strategies, adding sintering aid is the most investigated. Al_2O_3 , Fe_2O_3 , Li_2O , Cr_2O_3 , CoO , and so on, have been found to be effective sintering promoters for YSZ [7–19]. While some of them can reduce the sintering temperature of YSZ significantly, they may negatively affect the conductivity. The effect of sintering aids on the conductivity has to be considered because a reasonable ionic conductivity is necessary for YSZ used as the electrolyte of SOFCs. Radford and Bratton [7,8] reported that addition of 2 mol% Al_2O_3 or 5 mol% TiO_2 in CaO stabilized ZrO_2 (CSZ) improves the sinterability but reduces the conductivity. Verkerk et al. [9] investigated the effect of low concentrations of Fe_2O_3 , Al_2O_3 and Bi_2O_3 on the sintering behavior and electrical properties of $(\text{ZrO}_2)_{0.83}(\text{YO}_{1.5})_{0.17}$ and found that all these impurities can reduce the sintering temperature by 100–325 K but they all have negative influence on the conductivity. While most sintering aids decrease the ionic conductivity of YSZ, a proper amount of Al_2O_3 can not only reduce the sintering temperature but also improve the conductivity of YSZ through increasing the grain-boundary conductivity [10,11]. The improvement has been explained by that, the Al_2O_3 segregated at the grain boundary, scavenges the siliceous phase or promotes the atoms at the edge of YSZ grains to arrange in a disorder way to form an amorphous grain-boundary phase with high crystal defect concentration [10–13].

There have been some applications of Al_2O_3 -doped-YSZ as the electrolyte of SOFCs [11,13,16,17]. Ji et al. [11] reported that an electrolyte-supported SOFC with 4 wt.% Al_2O_3 -doped-YSZ electrolyte performs better than that with pure YSZ electrolyte. Hassan et al. [13] found that an addition of 0.77 wt.% Al_2O_3 to YSZ slightly improves the performance of a Ni–YSZ anode-supported SOFC fabricated by co-sintering the anode and electrolyte bi-layer at 1673 K for 5 h. Knibbe et al. [16] investigated the effect of 15 wt.% alumina addition on the Ni–YSZ anode/YSZ interface of electrolyte-supported SOFCs and indicated that NiAl_2O_4 is formed in the alumina regions in the electrolyte and it grows into the adjacent grain boundaries to form an interconnected NiAl_2O_4 network up to 4 μm deep into the electrolyte. While the NiAl_2O_4 may have not much detrimental effect on the performance of SOFCs operated at high temperatures (above 1123 K), it generally will negatively influence the SOFC performance operated at reduced temperatures because of significant grain-boundary resistance. Sui et al. announced that NiAl_2O_4 can be formed between NiO and Al_2O_3 at 1473 K and it decreases the performance of an electrolyte-supported SOFC with 4 wt.% Al_2O_3 -doped-YSZ electrolyte. This problem can be solved through introducing a buffer layer of pure YSZ between the alumina doped electrolyte and the Ni-based anode [17].

In this study, a pure YSZ buffer layer is applied between Ni–YSZ anode and alumina-doped YSZ electrolyte in fabricating anode-supported SOFCs, to avoid NiAl_2O_4 forming from direct contact of Ni and Al. The SOFCs with YSZ of different amount of alumina addition are investigated and the effect of the dopants on SOFC performance is presented and analyzed.

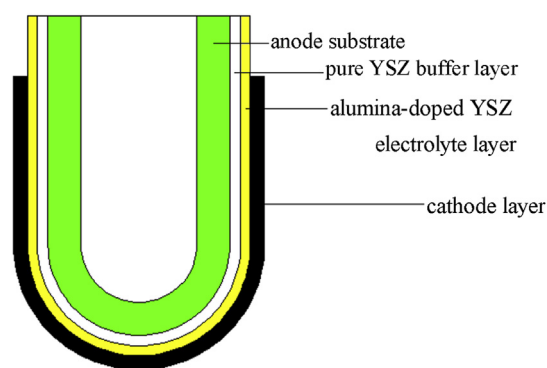


Fig. 1. A schematic illustration of the as-prepared SOFC.

2. Experimental

2.1. Preparation of slurries for buffer layer and electrolyte

The electrolyte film of the anode-supported SOFCs is prepared by dip-coating technique as detailed in our previous work [4,5]. Slurries of pure YSZ (Tosoh, Japan, mean particle size: 0.78 μm) and YSZ with different amount of Al_2O_3 (Xinfumeng, China, α -phase, mean particle size: 1.19 μm) (1 wt.%, 3 wt.%, 5 wt.%, 7 wt.%, regarding to the amount of YSZ) were respectively prepared by mixing powder (20 g YSZ and 0–7 wt.% Al_2O_3) with 57 g ethanol as solvent, 0.57 g triethanolamine (TEA) as dispersant, 0.82 g polyvinyl butyral (PVB) as polymer binder, 0.74 g di-2-ethylhexyl phthalate (DOP) and 0.74 g polyethylene glycol-600 (PEG-600) as plasticizers, and ball milling for 3 h.

2.2. Preparation of anode-supported SOFCs

To fabricate anode-supported SOFCs for the present investigation, some tubular anode substrates were prepared, also by dip-coating technique [4,5]. 5 g PVB was dissolved in 20 g ethanol to get a PVB solution. 18 g NiO powder (Inco, Canada) and 18 g YSZ were mixed with 4 g graphite as pore former, 20 g ethanol as solvent and 1.5 g TEA as dispersant. The mixture was ball milled for one hour. 25 g PVB solution functioning as binder, 3 g PEG-600 and 3 g DOP as plasticizer were added into the mixture and the ball milling was continued for two hours to get anode slurry. A glass rod, used as a mould, was then vertically dipped into the anode slurry. After 5 s, the glass rod was drawn out from the slurry, followed by drying for 10 min in air to form a layer of NiO–YSZ on the glass rod. The dip coating process was repeated 8 times to obtain required thickness of the layer. After drying in air at room temperature for 12 h, a green tubular anode substrate was formed and removed from the glass rod and then pre-fired at 1373 K for 2 h. The length of the tube is 3.0 cm and the diameter is 1.0 cm.

The pre-fired anode substrates were coated with a first layer of pure YSZ as buffer layer, followed by a second layer of pure YSZ or alumina-doped YSZ electrolyte. For the first layer, the anode substrates were dipped into the YSZ electrolyte slurry. After 2 s, the anode was taken up and dried with a hair dryer. The same process was performed in coating the second layer, respectively with pure YSZ, and 1, 3, 5, and 7 wt.% Al_2O_3 -doped-YSZ slurries. Those anode-supported coatings with pure YSZ electrolyte were respectively sintered at 1673 K, 1623 K, and 1573 K for 4 h. Those with 1–7 wt.% alumina-doped electrolyte were sintered at 1623 K and 1573 K for 4 h, respectively. Moreover, some of the pre-fired anode substrates were dipped into the slurry with 1 wt.% alumina doping twice (without pure YSZ buffer layer) and then sintered at 1573 K for 4 h.

At last, cathode layer was applied on the electrolyte. $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM, Ningbo Institute of Physical Chemistry) was mixed with YSZ (Tosoh) in a weight ratio of 1:1. The mixed powder and binder (terpineol: PVB = 9:1 in weight) in a weight ratio of 1:1.5 was ground for 1 h to obtain a stable composite cathode paste. The paste was applied onto the YSZ electrolyte film by brush painting and then sintered at 1373 K for 2 h.

A schematic illustration of the as-prepared SOFC is shown in Fig. 1.

2.3. Cell assembling and testing

Each single tubular SOFC was attached to one end of an alumina tube by using silver paste as sealing and joining material [20,21]. The single cell was tested at different temperatures using humidified hydrogen (3% water, 60 ml min^{-1}) as fuel and ambient air as oxidant. The cell performance and impedance spectra were measured using IviumStat electrochemical analyzer (Ivium Technologies B.V., Netherlands). A four-probe setup was adopted to eliminate the resistance losses from the current leading wires. The cell current–voltage (I – V) characteristics were tested by linear sweep voltammetry at a scanning rate of 5 mV s^{-1} . The impedances were measured in the frequency range of 100 kHz–0.1 Hz with signal amplitude of 5 mV under open circuit condition. After the electrochemical test, the cells were fractured and examined using a scanning electron microscope (SEM, Hitachi S-3700).

3. Results and discussion

3.1. Sintering behavior of the electrolytes

A dense electrolyte layer is essential for high performance SOFCs. If the electrolyte is not dense or in other words, not well sintered, some oxidant (oxygen in air or pure oxygen) will diffuse across the electrolyte to the anode side (fuel chamber), increasing the oxygen partial pressure of the anode. According to Nernst equation, the open circuit voltage (OCV) of a SOFC operating with O_2 oxidant and H_2 fuel is

$$V_{\text{OCV}} = \frac{RT}{4F} \ln \frac{p_{\text{O}_2, \text{cathode}}}{p_{\text{O}_2, \text{anode}}} \quad (1)$$

where F is the Faraday constant, T the temperature, R the gas constant, and $p_{\text{O}_2, \text{cathode}}$ and $p_{\text{O}_2, \text{anode}}$ are the oxygen partial pressure of the cathode and the anode, respectively. Obviously, a higher oxygen partial pressure at the anode $p_{\text{O}_2, \text{anode}}$ results in a lower OCV, leading to lower performance of SOFC. Therefore, a good sinterability of the electrolyte is very important to the performance of SOFCs.

Sintering behavior of bulk ceramics is usually characterized by relative density or porosity. However, in the present work, the electrolyte is a ceramic film, with a thickness of only about $20 \mu\text{m}$, supported by an anode substrate. It is very difficult to measure the relative density of the electrolyte film with conventional methods, such as Archimedes and mercury intrusion methods. Gas Transmission Rate (GTR), defined as the quantity of a given gas passing through a unit of the parallel surfaces of a film in unit time, has been commonly applied to characterize gas permeability of plastic films, can be used to characterize the densification of the electrolyte films. For the present work, GTR can be calculated through the following formula:

$$\text{GTR} = \frac{(p_{\text{O}_2, \text{anode}} - p_{\text{O}_2, \text{anode}}^0) \times r_{\text{anode}}}{p_0 A} \quad (2)$$

Here, $p_{\text{O}_2, \text{anode}}^0$ is the equilibrium oxygen partial pressure of the reaction of H_2 and O_2 . It is also the oxygen partial pressure of the anode when the SOFC is operated at a theoretical OCV, in the case that the electrolyte is completely dense. r_{anode} is the gas flow rate of the fuel (60 ml min^{-1}), p_0 is the standard atmospheric pressure (1 atm or 10^5 Pa), and A is the surface area of the cell electrolyte ($\sim 2 \text{ cm}^2$).

Fig. 2 shows the OCVs of the SOFCs with electrolytes of pure YSZ and YSZ doped with different amount of alumina, sintered at different temperatures, operated at 1073 K. The corresponding GTRs are also shown. Obviously, there are strict corresponding relations between the OCVs and the GTRs. Higher GTR corresponds to lower OCV, which is reasonable, as explained above.

Generally, an OCV of over 1 V is expected to a SOFC for practical use. Fig. 2 shows that the OCV of the cell with pure YSZ electrolyte sintered at 1673 K is about 1.04 V, very close to the theoretical expectation ($\sim 1.1 \text{ V}$), implying that the electrolyte is reasonably dense. A GTR value of $1.3 \times 10^{-22} \text{ mol m}^{-1} \text{ s}^{-1}$ is calculated according to Eq. (2). With lower sintering temperatures, 1623 K and 1573 K, the OCVs of the cells with pure YSZ electrolytes are only 0.95 V and 0.79 V, corresponding to GTRs of 6.4×10^{-20} and $6.5 \times 10^{-17} \text{ mol m}^{-1} \text{ s}^{-1}$, respectively. The gas leaking rates are 2 and 5 orders higher than that of the relatively dense electrolyte sintered at 1673 K, indicating that pure YSZ electrolyte sintered at temperatures lower than 1673 K is not dense enough for practical use.

The OCVs of the cells with 1 wt.% and 3 wt.% alumina-doped electrolyte sintered at 1623 K are 1.03 V and 1.02 V respectively, with similar GTRs to that of the cell with pure YSZ sintered at 1673 K, suggesting that Al_2O_3 addition may improve the sinterability of YSZ. However, with more Al_2O_3 doping, 5 wt.% and 7 wt.%, the OCVs of cells decrease to 0.96 V and 0.8 V, with gas leaking rates increasing in 1 and 4 orders, respectively. Similarly, the OCV of the cell with 1 wt.% alumina-doped electrolyte sintered at 1573 K is 1.05 V, while the OCVs of the cells with more Al_2O_3 doping electrolyte (3 wt.% and 5 wt.%) drop to 0.92 V and 0.51 V, respectively. There are four electrolytes enabling the SOFCs to have OCVs of over 1 V. They are (noted by alumina wt.%/sintering temperature): 0 wt.%/1673 K (S1), 1 wt.%/1573 K (S2), 1 wt.%/1623 K (S3) and 3 wt.%/1623 K (S4). An optimum doping percentage range is most likely between 1 wt.% and 3 wt.%, which can reduce the sintering temperature by at least 50 K.

It is generally recognized that a dilute impurity addition (within its solubility in the main crystal) into the substrate may enhance the densification during sintering because the impurity may cause

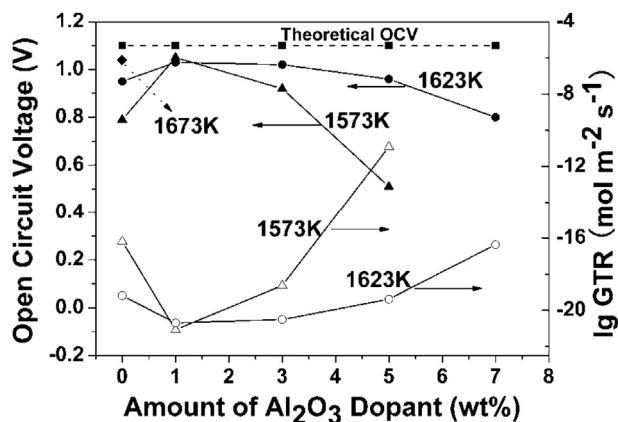


Fig. 2. Open circuit voltages (OCVs) and Gas transmission rates (GTRs) of SOFCs with pure YSZ and Al_2O_3 -doped-YSZ electrolytes, sintered at different temperatures.

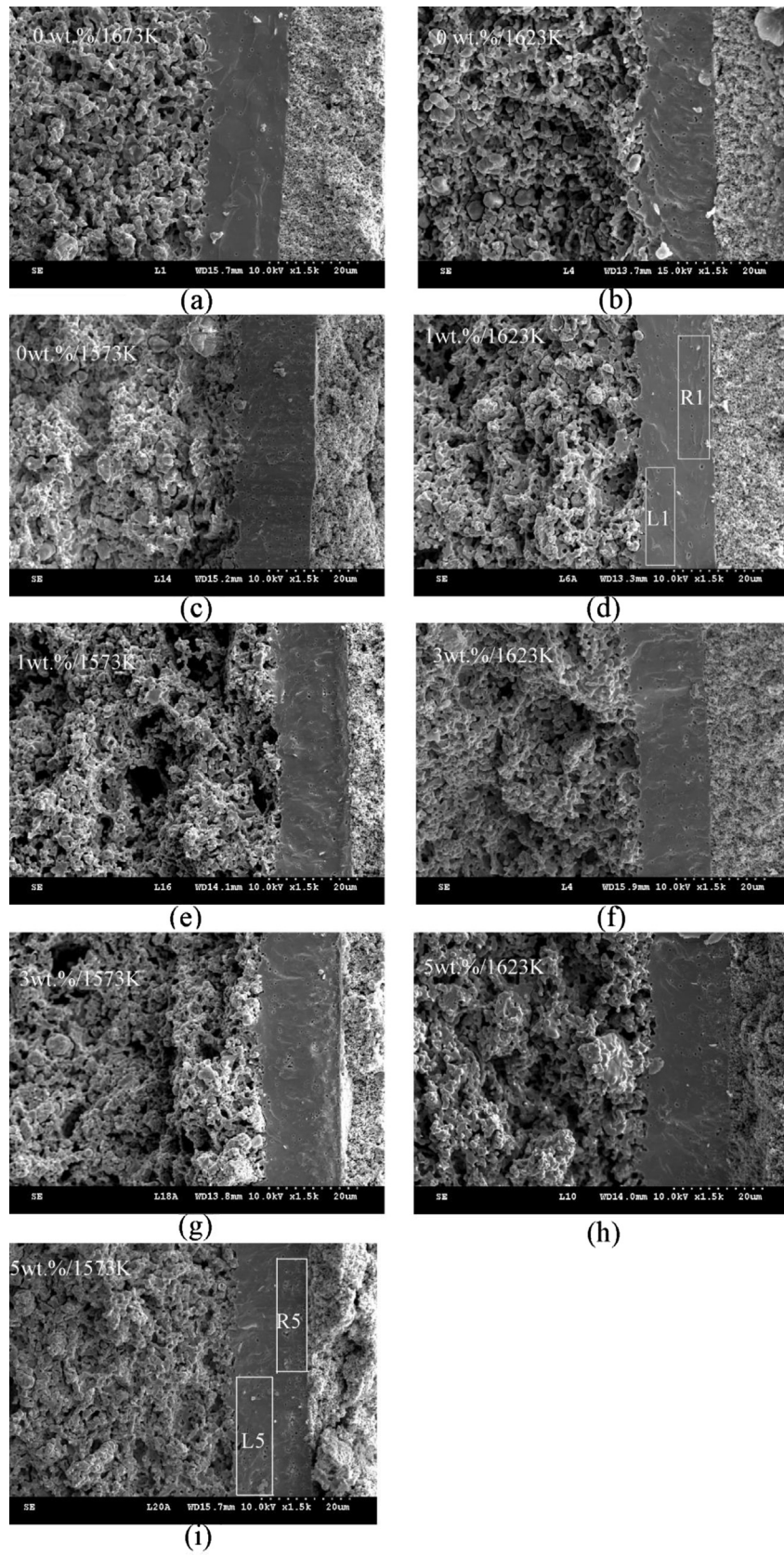


Fig. 3. SEM images of the sectional microstructure of the cells.

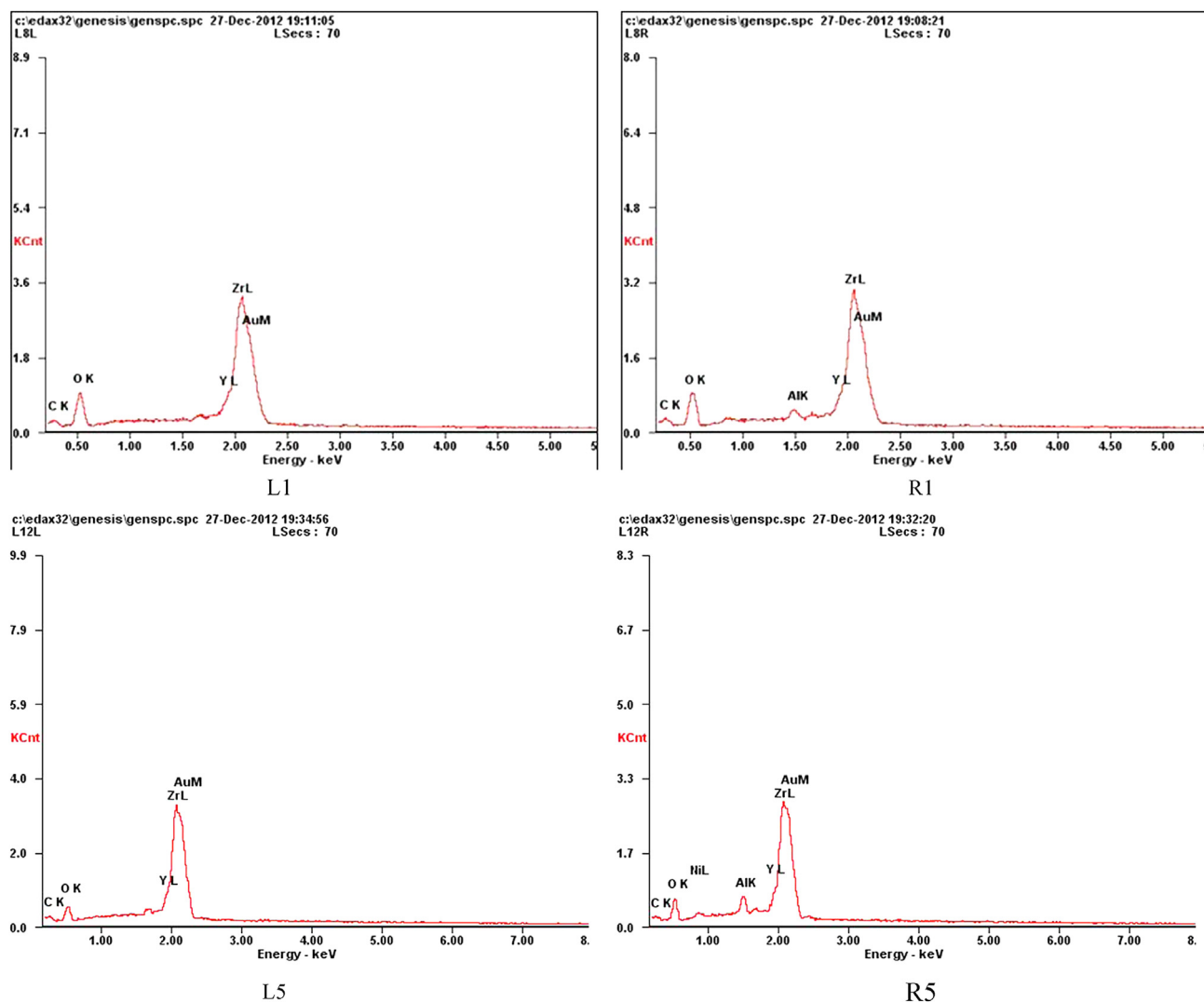


Fig. 4. EDX results showing there are no aluminum elements existing in the pure YSZ buffer layers.

increase of point defects to promote the diffusion effect [22]. The ionic size of Al^{3+} (0.53 Å) is much smaller than that of Zr^{4+} (0.84 Å). The mismatch of ionic size leads to the low solubility of alumina in YSZ, only 0.6 mol% (~ 0.48 wt.%) when sintered at 1773 K [25] and 0.1 mol% (~ 0.08 wt.%) when sintered at 1573 K [6], far below the doping amount in the present work (>1 wt.%). Thus alumina mainly distribute on the grain boundary. According to the previous researches by Guo et al. [10] and Ji et al. [11], the surplus alumina segregated at grain boundaries may enhance the diffusion or mobility of the boundaries. When a proper amount of alumina is added to YSZ (such as 1–3 wt.% in the present work), an improved sinterability may be obtained due to the enhanced grain boundary mobility.

Consequently, the densification improvement is caused by the interaction of alumina and YSZ and there is an optimal concentration of the interaction sites where alumina dissolves and segregates. To reach the optimal condition, smaller amount of alumina is needed if the alumina particles are finer and well distributed in YSZ. Matsui et al. studied the sintering behavior of fine zirconia powders with alumina added (≤ 1 wt.%) by powder mixing and chemical processes and found that the densification is more stimulated by the chemical processes which lead to a homogeneously distribution of the addition [23]. Note that in the present study, YSZ

and α -phase alumina powders purchased from Tosoh and Xinfumeng, with mean particle size of 0.78 and 1.19 μm , respectively, are specially used by powder mixing. Hassan et al. [13] reported that an optimal Al_2O_3 (Fluka, Switzerland) amount doped YSZ (Tosoh) to obtain low leak rates is in the region of 0.7–1.0 wt.% and the leak rates become larger with more Al_2O_3 (2–4 wt.%). Ji et al. [11] showed that 3–4 wt.% Al_2O_3 (Beijing Construction Material Institute)-doped YSZ (Beijing Construction Material Institute) is the densest. The optimal Al_2O_3 amount varies in different research, which may be due to the differences of particle size, crystal phase and impurity of raw materials, along with the ways of introducing the dopants. Nevertheless, large Al_2O_3 particles should be excluded as they will occupy much volume fraction of YSZ and result in low performance.

Shown in Fig. 3 are the cross section microstructure images of the cells. From Fig. 3a, b and c, it can be seen that pure YSZ electrolyte sintered at 1673 K (0 wt.%/1673 K) is dense with only some small closed pores, while with decreasing sintering temperature, more and more porous appear. When 1 wt.% of Al_2O_3 is added, the YSZ electrolytes sintered at 1623 K (1 wt.%/1623 K) (Fig. 3d) and 1573 K (1 wt.%/1573 K) (Fig. 3e) are both denser than the pure YSZ sintered at 1623 K (Fig. 3b), reflecting the effectiveness of Al_2O_3 as sintering aid. There is no obvious interface between the pure YSZ

and alumina-doped-YSZ layers. As more Al_2O_3 is doped into YSZ electrolyte (3 wt.% and 5 wt.%), the alumina-doped electrolyte layer, especially the region close to the surface (or the electrolyte–cathode interface), is very porous. It has been demonstrated that as the alumina doping amount is far apart from the optimum value, the doping will give a negative influence on the sinterability of YSZ [11]. As can be seen, 1 wt.% alumina is the most effective doping percentage, which can reduce the sintering temperature of YSZ by 100 K. With the doping percentage increasing to 5 wt.%, the alumina-doped-YSZ is even more porous than pure YSZ. These results are well consistent with the density characterization based on the gas transmission rate analysis of the electrolyte membrane.

Fig. 4 shows the results of EDX analysis of L1 area (pure YSZ buffer layer of 1 wt.%/1623 K) and R1 area (alumina-doped YSZ layer of 1 wt.%/1623 K) in Fig. 3d, L5 area (pure YSZ buffer layer of 5 wt.%/1573 K) and R5 area (alumina-doped YSZ layer of 5 wt.%/1573 K) in Fig. 3i. The EDX analysis of R1 and R5 areas indicates that Al element is found in both these two areas (Al_2O_3 -doped-YSZ layer), which is reasonable. While, Al is not found in L1 and L5 areas (pure YSZ buffer layer), which suggests that with 1–5 wt.% alumina doping in the alumina-doped YSZ layer, the pure YSZ buffer layer can effectively avoid the infiltration of Al_2O_3 to anode.

Note that, as alumina doping amount increases to 3 wt.% and 5 wt.%, the YSZ buffer layers (contacting the Al-contained electrolyte layer) are denser than the pure YSZ electrolyte (without any Al surrounded) sintered at the same temperature (Comparing Fig. 3e, g and i to Fig. 3c). As no aluminum is detected in the buffer layer, the densification cannot be contributed to alumina as sintering promoter. There has been evidence in our experiment showing that alumina tends to migrate to the surface of Al_2O_3 -doped-YSZ bulk, meaning that the surface free energy of alumina is lower than that of YSZ or lower than the interface free energy between Al_2O_3 and YSZ, resulting in no alumina diffusing to the pure YSZ buffer layer. A lower surface energy of Al_2O_3 enables alumina in the electrolyte to attract pores during sintering, resulting in densification of the pure YSZ buffer layer, because pores in the buffer layer tends to accumulate at the alumina-doped electrolyte.

3.2. Electrical performance

Fig. 5a shows the typical performance of each kind of cells with OCVs of over 1 V, operated at 1073 K. For each kind of cells, a group of at least three samples were fabricated and tested. The performance of the cells in the same group varies but not much, showing a reasonable reproducibility of the cell fabrication. The average values of maximum power density for every group of cells are shown in Fig. 5b, with error bars representing the experimental difference of measurements. The cell with 1 wt.% alumina-doped YSZ electrolyte sintered at 1573 K (1 wt.%/1573 K, S2) reveals the highest maximum power density of 684 mW cm^{-2} , while the one sintered at 1623 K (1 wt.%/1623 K, S3) gives the second highest output of 463 mW cm^{-2} , which is larger than that with pure YSZ electrolyte sintered at 1673 K (0 wt.%/1673 K, S1), 429 mW cm^{-2} . The cell with 3 wt.% alumina-doped YSZ electrolyte sintered at 1623 K (3 wt.%/1623 K, S4) gives the lowest output, 253 mW cm^{-2} . Furthermore, the cell with 1 wt.% alumina-doped YSZ electrolyte but without YSZ buffer layer, sintered at 1573 K (1 wt.%/1573 K, without buffer layer, S5), is tested. Its OCV is larger than 1 V, and its maximum power density is 360 mW cm^{-2} , much smaller than the cell with the same electrolyte but also with YSZ buffer layer (S2).

A typical impedance spectrum of the cells under open-circuit condition is shown in Fig. 6a. The intercept of the real axis at high-frequency corresponds to ohmic resistance of the cell, while the real axis range covered by the arc at lower frequency region represents the overall electrode polarization resistance, including

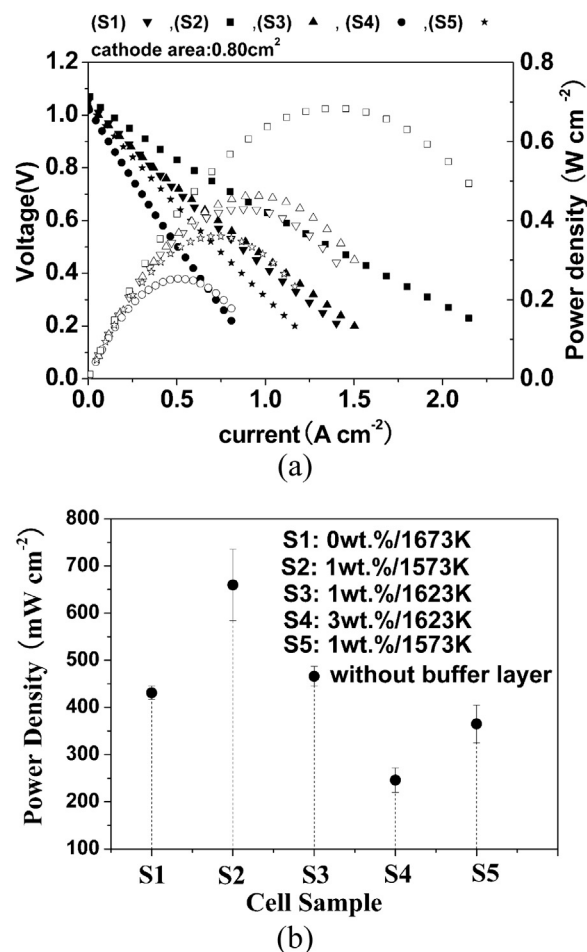


Fig. 5. Performances of the different kinds of cells operated on humidified hydrogen as fuel and ambient air as oxidant, at 1073 K: (a) voltage and power density versus current density for typical cells. (b) Average values of maximum power densities for each group of cells.

both the anode and cathode polarization resistances. The total resistance is the sum of the ohmic resistance and the polarization resistance. All the resistances of the measured cells are presented in terms of area specific resistances (ASR, $\Omega \text{ cm}^2$) and are shown in Fig. 6b. As we can see, the total resistance of the cell with 1 wt.% alumina-doped YSZ electrolyte sintered at 1573 K (S2) is the smallest ($0.59 \Omega \text{ cm}^2$) and that of the cell with 3 wt.% alumina-doped YSZ electrolyte sintered at 1623 K (S4) is the largest ($1.18 \Omega \text{ cm}^2$).

The ohmic resistance of a cell is the sum of the ohmic resistances of the anode, the buffer layer, the electrolyte layer, the cathode, and the contacts (interfaces) between each two adjacent layers. As the preparation of cathode for all the cells is the same, the performance differences of the cells are seldom related to the cathode. Comparing the ohmic resistances of the cells with buffer layer, it is found that the ohmic resistances of the cell with 1 wt.% alumina-doped YSZ electrolyte sintered at 1573 K (S2: $0.39 \Omega \text{ cm}^2$) and 1623 K (S3: $0.50 \Omega \text{ cm}^2$) are similar to that of the cell with pure YSZ electrolyte sintered at 1673 K (S1: $0.45 \Omega \text{ cm}^2$), while for the cells with 3 wt.% alumina sintered at 1623 K (S4) and 1 wt.% alumina sintered at 1573 K but without buffer layer (S5), the ohmic resistances are much larger, over $0.8 \Omega \text{ cm}^2$, almost twice that of S2.

Some previous research has shown that small amount of alumina doping increases the conductivity of YSZ through increasing the grain-boundary conductivity [10,11,23]. However,

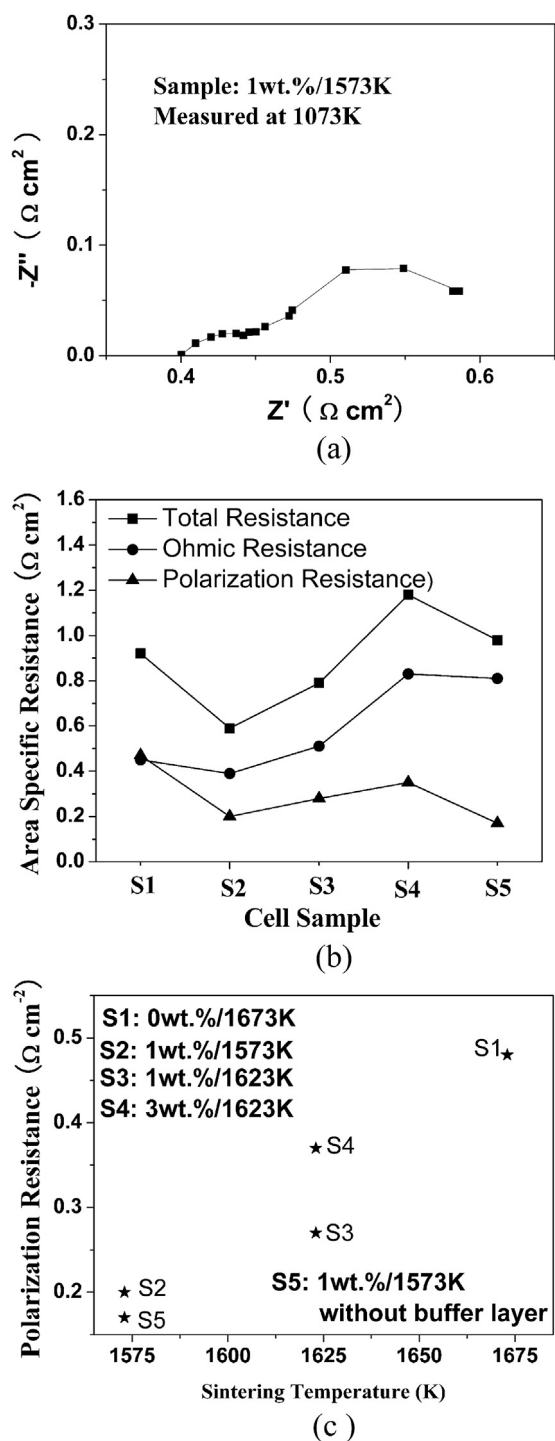


Fig. 6. Electrical properties of the cells: (a) a typical electrochemical impedance spectrum of the cells measured at 1073 K; (b) ohmic, polarization, and total resistances of the cells; (c) polarization resistance vs. sintering temperature of electrolytes.

when too much alumina is introduced into YSZ, the diffusion paths of oxygen ion vacancies will be blocked by the insulating alumina, without oxygen ion vacancies, segregated at the grain boundaries. This can explain the observed phenomena that, in some conditions, the ohmic resistance of YSZ with 1 wt.% alumina doping is slightly lower than that of pure YSZ, while the ohmic resistance of 3 wt.% Al_2O_3 -doped-YSZ is much larger.

With identical alumina doping amount (1 wt.%) and the same sintering temperature (1573 K), the cell without buffer layer has a

much higher ohmic resistance ($0.81 \Omega \text{ cm}^2$) than that of the cell with buffer layer. As described in the experimental part, the cell with buffer layer is with a pure YSZ layer and an alumina-doped-YSZ layer (Y + A), and the cell without buffer layer is with two alumina-doped-YSZ layers (A + A). It has been shown that the ohmic resistance of the 1 wt.% alumina-doped-YSZ (A) is similar to that of pure YSZ (Y), suggesting the ohmic resistance of Y + A should be close to that of A + A. As the cathode and anode conditions of the two cells are the same, then the difference between the ohmic resistances of the two cells should be from the anode/YSZ and anode/ Al_2O_3 -doped-YSZ interfaces. It has been reported that in NiO-YSZ anode-supported SOFCs, NiO can diffuse into YSZ electrolyte [16,24,26]. When alumina is doped in the electrolyte, NiO will react with Al_2O_3 to form nonconducting NiAl_2O_4 , which can not be completely reduced in hydrogen at operating temperatures of SOFC [16], resulting in high ohmic resistance of the cell. Thus, combined with the EDX analysis above, it has been demonstrated that a pure YSZ buffer layer is effective in avoiding the formation of NiAl_2O_4 .

It turns out that the polarization resistance of the cells is positively correlated to the sintering temperature, as shown in Fig. 6c. Polarization resistance of a SOFC is determined by the electrochemical activities of the electrodes. A proper porosity is necessary for an electrode so that sufficient triple phase boundaries (TPBs, phases of gas, ionic conduction and electronic conduction) can be provided to activate the electrochemical reactions occur in electrode, thus to reduce the polarization resistance. High sintering temperature may cause either of the electrodes over-sintered, leading to low porosity, thus to large polarization resistance. As the cathodes of all the cells were sintered at the same temperature (1373 K), the lower polarization resistances of the cells S2 and S5 should be attributed to the reduced sintering temperature (1573 K, compared to the commonly applied 1673 K) which prevents the anodes from over-sintering.

To sum up: Among the electrolytes corresponding to the four cells with OCVs of over 1 V, the 1 wt.% Al_2O_3 -doped-YSZ electrolyte sintered at 1573 K reveals the highest SOFC performance and the lowest resistance. In Fig. 7, a 12 h stable operation at OCV of 1.05 V also suggests that the 1 wt.% Al_2O_3 -doped-YSZ electrolyte sintered at 1573 K is dense enough for practical use.

4. Conclusion

A proper amount of Al_2O_3 doping can effectively reduce the sintering temperature of YSZ thin electrolyte for anode-supported SOFCs. In the present study, it turns out that 1 wt.% Al_2O_3 is the

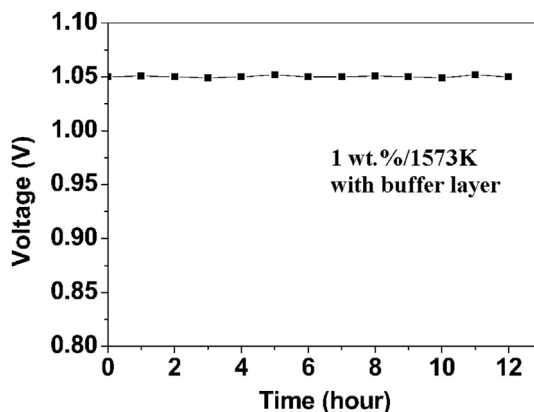


Fig. 7. Stability of the cell with 1 wt.% alumina-doped YSZ electrolyte (with buffer layer) sintered at 1573 K, under open circuit.

optimum amount of doping and it reduces the sintering temperature of YSZ from 1673 K to 1573 K. A pure YSZ buffer layer can effectively prevent the Al_2O_3 from contacting the Ni-based anode to form electrically insulated NiAl_2O_4 at the interface of anode and electrolyte. The single cell with 1 wt.% alumina-doped YSZ electrolyte sintered at 1573 K reveals higher output of 684 mW cm^{-2} than the conventional cell with pure YSZ electrolyte sintered at 1673 K (429 mW cm^{-2}). AC impedance results verify that the polarization resistance of the former cell is decreased due to lower sintering temperature, which can avoid anode over-sintering. Consequently, higher performance and lower cost anode-supported SOFCs can be realized by doping a proper amount of Al_2O_3 into the YSZ electrolyte and introducing a pure YSZ buffer layer between the Ni-based anode and the Al-contained electrolyte.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2013.10.023>.

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